

What is claimed is:

1. A manufacturing method for a single crystal of calcium fluoride, having its optical properties improved through an annealing process comprising the steps of:

providing a single crystal of calcium fluoride in a sealable container, sealing said container with a vacuum, then

heating said container with a heater arranged external to said container such that a temperature inside said container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride,

maintaining the temperature inside said container at said first temperature for a designated period of time,

lowering the temperature inside said container to room temperature,

wherein,

the first temperature is between 1020 °C to 1150 °C.

2. A manufacturing method according to claim 1, wherein the step of lowering the temperature comprises decreasing the temperature from said first temperature to room temperature at a rate of 2 °C/hour or less.

3. A manufacturing method according to claim 1, wherein the step of lowering the temperature comprises decreasing the temperature from said first temperature to a second temperature, which is in the range of around 600 °C to 900 °C , at a rate of 2 °C/hour or less.

4. A manufacturing method according to claim 3, wherein the step of lowering the temperature comprises decreasing the temperature from said second temperature to room temperature at a rate of 5 °C/hour or less.
5. A manufacturing method according to claim 1, wherein a single crystal of calcium fluoride with a diameter of  $\varnothing$  200 mm or greater, which can be used in an optical system for photolithography, can be obtained.
6. A manufacturing method according to claim 5, wherein a single crystal of calcium fluoride with a difference in the refractive index,  $\Delta n$ , equal to  $2 \times 10^{-6}$  or less can be obtained.
7. A manufacturing method according to claim 5, wherein a single crystal of calcium fluoride with a double refraction value, in a direction of the axis of light, of 2 nm/cm or less can be obtained.
8. A manufacturing method according to claim 5, wherein a single crystal of calcium fluoride with a double refraction value, in an off-axis direction perpendicular to the axis of light, of 5 nm/cm or less can be obtained.
9. A manufacturing method for a single crystal of calcium fluoride having its optical properties improved comprising the steps of:
- providing a single crystal of calcium fluoride and a fluorination agent in a second

container arranged in a sealable first container, sealing said first container with a vacuum, then

heating said first container with a heater arranged external to said first container such that a temperature inside said second container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride, while said second container is filled with a fluorine gas atmosphere,

maintaining the temperature inside said second container at the first temperature for a designated period of time,

lowering the temperature inside said first container and the temperature inside said second container to room temperature,

opening the inside of said first container to a normal atmosphere,

wherein,

the first temperature is between 1020 °C and 1150 °C.

10. A manufacturing method according to claim 9, wherein the step of lowering the temperature comprises decreasing the temperature from said first temperature to room temperature at a rate of 2 °C/hour or less.

11. A manufacturing method according to claim 9, wherein the step of lowering the temperature comprises decreasing the temperature from said first temperature to a second temperature, which is in the range of around 600 °C to 900 °C, at a rate of 2 °C/hour or less.

12. A manufacturing method according to claim 11, wherein the step of lowering the

temperature comprises decreasing the temperature from said second temperature to room temperature at a rate of 5 °C/hour or less.

13. A manufacturing method according to claim 9, wherein a single crystal of calcium fluoride with a diameter of  $\varnothing$  200 mm or greater, which can be used in an optical system for photolithography, can be obtained.

14. A manufacturing method according to claim 13, wherein a single crystal of calcium fluoride with a difference in the refractive index,  $\Delta n$ , equal to  $2 \times 10^{-6}$  or less can be obtained.

15. A manufacturing method according to claim 13, wherein a single crystal of calcium fluoride with a double refraction value, in the direction of the axis of light, of 2 nm/cm or less can be obtained.

16. A manufacturing method according to claim 13, wherein a single crystal of calcium fluoride with a double refraction value, in the off-axis direction perpendicular to the axis of light, of 5 nm/cm or less can be obtained.

17. A single crystal of calcium fluoride for photolithography, having a wavelength of 250 nm or less, with a diameter of  $\varnothing$  200 mm or greater, with a double refraction value, in the direction of the axis of light, that is 2 nm/cm or less.

18. A single crystal of calcium fluoride according to claim 17, wherein the double refraction value in the off-axis direction perpendicular to the axis of light is 5 nm/cm or less.

19. A single crystal of calcium fluoride according to claims 17 or 18, wherein a difference in a refractive index,  $\Delta n$ , is  $2 \times 10^{-6}$  or less.

20. A manufacturing method for a single crystal of calcium fluoride, having its optical properties improved comprising the steps of

providing a single crystal of calcium fluoride in a sealable container, sealing said container with a vacuum, then

heating said container with a heater arranged external to said container such that a temperature inside said container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride,

maintaining the temperature inside said container at said first temperature for a designated period of time,

lowering the temperature inside said container to room temperature,

wherein,

a balance between an effect of improving the optical properties of said single crystal of calcium fluoride and the productivity, including delivery time and cost, is achieved, such that, during a high temperature range, the temperature is lowered at a slow rate, and during a low temperature range that is lower than the high temperature range, the temperature is lowered faster as the temperature becomes lower.

21. A manufacturing method for a single crystal of calcium fluoride, having its optical properties improved comprising the steps of:

providing a single crystal of calcium fluoride in a sealable container, sealing said container with a vacuum, then

heating said container with a heater arranged external to said container such that a temperature inside said container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride,

maintaining the temperature inside said container at said first temperature for a designated period of time,

lowering the temperature inside said container to room temperature,

wherein,

said container is filled with an inert gas, and the inside of said container is maintained at an atmosphere of approximately 1 atm such that said single crystal of calcium fluoride is not oxidized.

22. A manufacturing method for a single crystal of calcium fluoride having its optical properties improved comprising the steps of:

providing a single crystal of calcium fluoride and a fluorination agent in a second container arranged in a sealable first container, sealing said first container with a vacuum, then

heating said first container with a heater arranged external to said first container such that the temperature inside said second container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride, while said second container is filled with

a fluorine gas atmosphere,

maintaining the temperature inside said second container at the first temperature for a designated period of time,

lowering the temperature inside said second container to room temperature, and

opening the inside of said first container to a normal atmosphere,

wherein,

at a minimum, in order to prevent oxidation of said single crystal of calcium fluoride during the process, the process is carried out such that said fluorination agent is vaporized and becomes a fluorine gas atmosphere inside of said second container, while a pressure inside said first container is maintained at approximately 1 atm.

23. A manufacturing method for a single crystal of calcium fluoride having its optical properties improved comprising the steps of:

maintaining said single crystal of calcium fluoride at a maximum first temperature which is within the range of 1020 °C to 1150 °C, for a designated period of time, and

lowering the temperature of said single crystal of calcium fluoride to a second temperature, which is in the range of around 600 °C to 900 °C, at a rate of 1.2 °C/hour or less.

24. A manufacturing method according to claim 23, wherein the step of lowering the temperature comprises decreasing the temperature from said second temperature to a third temperature, which is in the range of around 400 °C to 600 °C, at a rate of 3 °C/hour or less.

25. A manufacturing method according to claim 24, wherein the step of lowering the temperature comprises decreasing the temperature from said third temperature to room temperature at a rate of 5 °C/hour or less.

26. A manufacturing method for a single crystal of calcium fluoride, having its optical properties improved comprising the steps of:

providing a single crystal of calcium fluoride in a sealable container, sealing said container with a vacuum, then

heating said container with a heater arranged external to said container such that a temperature inside said container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride,

maintaining the temperature inside said container at the first temperature for a designated period of time,

lowering the temperature inside said container to room temperature,

wherein,

the first temperature, which is between 1020 °C and 1150 °C, is lowered to a second temperature, which is in the range of around 600 °C to 900 °C, at a rate of 1.2 °C/hour or less.

27. A manufacturing method according to claim 26, wherein the step of lowering the temperature comprises decreasing the temperature from said second temperature to a third temperature, which is in the range of around 400 °C to 600 °C, at a rate of 3 °C/hour or less.



28. A manufacturing method according to claim 27, wherein the step of lowering the temperature comprises decreasing the temperature from said third temperature to room temperature at a rate of 5 °C/hour or less.

29. A manufacturing method according to claim 26, wherein a single crystal of calcium fluoride with a diameter of  $\varnothing$  230 mm or greater, which can be used for the optical system for photolithography, can be obtained.

30. A manufacturing method according to claim 29, wherein a single crystal of calcium fluoride with a difference in the refractive index,  $\Delta n$ , equal to  $2 \times 10^{-6}$  or less can be obtained.

31. A manufacturing method according to claim 29, wherein a single crystal of calcium fluoride with a double refraction value, in a direction of the axis of light, of 2 nm/cm or less can be obtained.

32. A manufacturing method according to claim 29, wherein a single crystal of calcium fluoride with a double refraction value, in the off-axis direction perpendicular to the axis of light, of 5 nm/cm or less can be obtained.

33. A manufacturing method for a single crystal of calcium fluoride having its optical properties improved comprising the steps of:

providing a single crystal of calcium fluoride and a fluorination agent in a second

container arranged in a sealable first container, sealing said first container with a vacuum, then

heating said first container with a heater arranged external to said first container such that a temperature inside said second container is raised to a first temperature, which is lower than a melting point of said single crystal of calcium fluoride, while said second container is filled with a fluorine gas atmosphere,

maintaining the temperature inside said second container at said first temperature for a designated period of time,

lowering the temperature inside second container to room temperature,

opening the inside of said first container to a normal atmosphere,

wherein,

the first temperature is between 1020 °C and 1150 °C, and

the temperature is decreased from said first temperature to a second temperature, which is in the range of around 600 to 900 °C, at a rate of 1.2 °C/hour or less,

34. A manufacturing method according to claim 33, wherein the step of lowering the temperature comprises decreasing the temperature from said second temperature to a third temperature, which is in the range of around 400 to 600 °C, at a rate of 3 °C/hour or less.

35. A manufacturing method according to claim 34, wherein the step of lowering the temperature comprises decreasing the temperature from said third temperature to room temperature at a rate of 5 °C/hour or less.

36. A manufacturing method according to claim 33, wherein a single crystal of calcium fluoride with a diameter of  $\phi$  230 mm or greater, which can be used for the optical system for photolithography, can be obtained.
37. A manufacturing method according to Claim 36, wherein a single crystal of calcium fluoride with a difference in the refractive index,  $\Delta n$ , equal to  $2 \times 10^{-6}$  or less can be obtained.
38. A manufacturing method according to Claim 36, wherein a single crystal of calcium fluoride with a double refraction value, in a direction of the axis of light, of 2 nm/cm or less can be obtained.
39. A manufacturing method according to Claim 36, wherein a single crystal of calcium fluoride with a double refraction value, in the off-axis direction perpendicular to the axis of light, of 5 nm/cm or less can be obtained.
40. A single crystal of calcium fluoride for photolithography having a wavelength of 200 nm or less, with a diameter of  $\phi$  230 mm or greater, wherein a double refraction value, in a direction of the axis of light, is 2 nm/cm or less.
41. A single crystal of calcium fluoride according to Claim 40, wherein the double refraction value in an off-axis direction perpendicular to the axis of light is 5 nm/cm or less.

42. A single crystal of calcium fluoride according to Claims 40 or 41, wherein the difference in the refractive index,  $\Delta n$ , is  $2 \times 10^{-6}$  or less.

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